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Interface chemistry and thermoelectric characterization of Ti and TiO$_x$ contacts to MBE-grown WSe$_2$

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Abstract

WSe$_2$ has demonstrated potential for applications in thermoelectric energy conversion. Optimization of such devices requires control over interfacial thermal and electrical transport properties. Ti, TiO$_x$, and Ti/TiO$_x$ contacts to the MBE-grown WSe$_2$ are characterized by XPS and transport measurements. The deposition of Ti is found to result in W-Se bond scission yielding metallic W and Ti-Se chemical states. The deposition of Ti on WSe$_2$ in the presence of a partial pressure of O$_2$, which yields a TiO$_x$ overlayer, results in the formation of substoichiometric WSe$_{x}$ (x < 2) as well as WO$_x$. The thermal boundary conductance at Ti/WSe$_2$ contacts is found to be reduced for greater WSe$_2$ film thickness or when Au/TiO$_x$ interface is present at the contact. Electrical resistance of Au/Ti contacts is found to be higher than that of Au/TiO$_x$ contacts with no significant difference in the Seebeck coefficient between the two types of contact structures. This report documents the first experimental study of Ti/WSe$_2$ interface chemistry and thermoelectric properties.

1. Introduction

High-speed, high-density and wearable electronics are being integrated in our everyday lives. Nanoscale thermal management is crucial to enabling further miniaturization of electronic circuits. Thermionic energy conversion devices can be used for integrated cooling of high power electronic devices through refrigeration and active cooling [1–3]. They have also been proposed for thermal to electrical energy conversion. They operate in a similar fashion as thermoelectric modules. The main difference between thermoelectric modules and solid-state thermionic modules is that in the former, transport is diffusive, whereas in the latter, transport is ballistic. While interfaces are important in thermoelectric modules [4, 5], they are even more significant in thermionic devices due to their ballistic nature. Thermal and electrical contact resistances have been studied for a variety of material interfaces, yet the interfacial Seebeck coefficient, the relevant parameter for thermionic devices, is not commonly measured.

WSe$_2$ has attracted significant attention for its ultra-low thermal conductivity in both in-plane and cross-plane directions. First principle calculations yield an in-plane thermal conductivity value of 3.935 W m$^{-1}$ K$^{-1}$ for monolayer WSe$_2$ which is an order of magnitude lower than calculated values for MoS$_2$ [6]. In the cross-plane direction, the thermal conductivity has been reported to be as low as 0.05 W m$^{-1}$ K$^{-1}$ for WSe$_2$ thin films [7]. This ultra-low thermal conductivity makes the material a promising candidate for thermal to electrical energy conversion devices. In the in-plane direction WSe$_2$ is a candidate for thermoelectric energy conversion and in the cross-plane direction, several layers of WSe$_2$ could be stacked to form Van der Waals structures useful for 2D solid-state thermionic devices as proposed by Chen et al [8] and later formulated by Wang et al [9].

In this work we study electrical and thermal transport across metal-WSe$_2$-HOPG contacts as well as metal oxide-WSe$_2$-HOPG contacts. Both thermionic power generation and refrigeration are optimized
when high electrical conductivity is combined with low thermal conductivity to enable a large temperature gradient. The Seebeck coefficient in these devices is determined by the interfacial band alignment [9–11]. Regardless of the application, engineering of 2D thermionic devices, in addition to transistors and optoelectronic devices, requires a high degree of control over the thermal and electrical resistances at the metal contact/WSe$_2$ interface, which dominate the device properties at the nanoscale. Engineering electrical and thermal contact resistances requires an understanding of the chemical and electronic interactions at the interface.

While interface chemistry of Au, Cr, Ir, Ag, Cu, and Pd contacts to WSe$_2$ has been previously examined [12–16], no reports on the Ti/WSe$_2$ interface and its thermoelectric response exist to date. A number of studies have reported Ti contacts for WSe$_2$ transistors [17–20]. Ti is predicted to exhibit strong orbital overlap and covalent bonding with WSe$_2$ resulting in an ohmic contact [21], however Liu et al [18] and Fang et al [19] report low current ambipolar characteristics. Kim et al [17] have demonstrated that ion beam irradiation of WSe$_2$ prior to contact deposition, which causes Se vacancies, results in a drastic increase in p-type field effect mobility and on/off ratio. They speculate the observed improvement to be due to the formation of ohmic contacts as a result of defect-mediated Fermi level pinning near the valence band. A fundamental study of interface chemistry is necessary to gain insight into the discrepancies between theory and experiment and to better understand the effect of processing. In the work presented here, we characterize interface chemistry using x-ray photoelectron spectroscopy (XPS) of Ti, TiO$_x$, and Ti/TiO$_x$ contacts to WSe$_2$ grown by molecular beam epitaxy (MBE). Cross-plane thermoelectric properties, including thermal conductance, electrical conductance, and Seebeck coefficient, are also measured.

2. Materials and methods

Full details of the materials growth and characterization can be found in the supporting information (stacks.iop.org/2DM/7/045033/mmedia). In summary, WSe$_2$ samples for this work were grown on grade 1 high ordered pyrolytic graphite (HOPG) purchased from SPI [22]. The growth was conducted in the MBE module of a ScientaOmicron UHV system described elsewhere [23]. The substrate temperature during the growth was 550 °C, and the Se/W flux ratio was 7000:1. The first ~0.25 monolayer was grown using an interrupted growth method that has been reported elsewhere [24, 25, 26]. During this process the sample was constantly exposed to the Se flux, but the W shutter was cyclically open for 30 s and closed for 90 s. The deposited material was left to cool in a Se flux to a temperature of 250 °C and was then re-heated to the growth temperature and growth continued without interrupting the W flux. The sample was cooled to 250 °C in a Se flux and then cooled under vacuum to room temperature.

XPS was acquired in the Analysis module of the ScientaOmicron UHV system at a pass energy of 50 eV with a monochromated Al kα x-ray source having a photon energy of 1486.7 eV. After brief air exposure to mount a shadow mask, the sample was reloaded into the XPS chamber and Ti was deposited onto the sample in-situ. The titanium was evaporated at a rate of approximately 1 Å/min. Deposition rates and estimated thickness were determined by XPS. For oxide deposition, a pressure of $5 \times 10^{-6}$ mbar of ultra-high purity O$_2$ was maintained in the chamber during deposition. All samples were capped with 1–2 nm of Au in-situ to prevent oxidation in air upon removal from UHV. Additional Au was deposited ex-situ to enable time-domain thermoreflectance (TDTR) measurement and probe station measurements of cross-plane electrical resistance and Seebeck coefficient.

The thermal boundary conductance across the various structures was measured using TDTR, an optical pump–probe technique used frequently to extract interfacial resistances. More details about our experimental set up and specific analysis can be found in the supporting information. The experimental setup to measure the Seebeck coefficient is also shown in supporting information. A thermoelectric module was placed beneath the HOPG substrate to provide a vertical temperature gradient across the sample. The cross-plane Seebeck coefficient is obtained from the slope of a linear fit of $-\Delta V$ against $\Delta T$ using $S = -\Delta V/\Delta T = -(V_{Au} - V_{HOPG}) / (T_{Au} - T_{HOPG})$. Using four-point probe, the probe-to-sample contact resistance was eliminated, which in this case is orders of magnitude higher than the actual resistance of the sample.

3. Results and discussion

3.1. Interface chemistry

XPS acquired before and after the deposition of ~2 nm of pure Ti metal is shown in figure 1. In the W 4f spectrum in (a), it is clear that metallic W appears as a result of W-Se bond scission. The Ti 3p peak overlaps with the W 4f spectral region with an asymmetric peak centered 32.93 eV. The Se 3d and Ti 2p spectra exhibit broadening due to the presence of new chemical states attributed to the Ti + Se reaction products. TiSe$_2$ has been found to have an enthalpy of formation ($\Delta H_f^{298,K}$) of $-222 \pm 42$ kJ mol$^{-1}$ which is significantly lower than that of WSe$_2$ which is reported to be $-185.5 \pm 5.5$ kJ mol$^{-1}$ [27]. Values of $\Delta H_f^{298,K}$ ranging from $-352 \pm 7.0$ to $-345 \pm 2$ kJ mol$^{-1}$ have been calculated for Se/Ti stoichiometries ranging from 2 to 1.80 [28]. The binding energy of TiSe$_2$ is reported to be at 456 eV in the Ti 2p spectrum and 54.3 eV in the Se 3d spectrum [29]. It
is apparent in the Se 3d spectrum that at least one new chemical state is present in addition to W-Se. The core level shift that occurs in the W 4f peak of WSe₂ following the deposition of Ti is within the error margins of 0.05 eV indicating no significant band bending. This is expected since the work function of Ti is ~ 4.3 eV and therefore lines up with the expected Fermi-level position of MBE grown WSe₂ [30].

Figure 2(a) shows XPS acquired before and after the deposition of TiOₓ. In this situation, the Ti 3p no longer over layers with the W 4f because the oxidation of the Ti shifts the features to higher binding energies. In the W 4f spectrum, a low binding energy shoulder is present indicating that a new chemical state has formed although it does not match the position of metallic W which was shown in figure 1. In the fit shown in figure 2(b), a low binding energy chemical state occurs at 31.64 eV. This is close to reported values of WSe₂ [31]. This suggests a higher reactivity of the WSe₂ surface with respect to MoS₂ and reemphasizes that process conditions require optimization for each individual TMDC material being investigated. We also observe the formation of WOₓ at 35.09 eV. In total, the W 4f signal reflects a composition of 90% WSe₂, 4% WSe₃, and 6% WOₓ. In other words, only 10% of the WSe₂ reacted during TiOₓ deposition. The formation of WSe₃ and WOₓ under a deposition pressure of 5 × 10⁻⁶ mbar has been previously reported by Smyth et al with the deposition of Ir on geological WSe₂ crystals [14]. They also identified the WOₓ chemical state after the deposition of Au in the absence of any interface reactions with WSe₂. This indicates that the formation of WOₓ occurs independently of W-Se bond scission in HV deposition conditions, likely at step edges. In the case of the deposition of a reactive metal, the metal is possibly catalyzing the oxidation reaction by breaking W-Se bonds, leaving W sites uncoordinated. We note that prior work on the oxidation of MoS₂ and WSe₂ has shown that the electronic properties of these materials can be influenced by this oxidation and further work is required to isolate the impact of such changes on our measurements [32, 33, 34].

The third type of interface created was a Ti/TiOₓ. First, 1.5 nm of TiOₓ were deposited on WSe₂. XPS acquired after this deposition is shown in figure 3 in red. The TiOₓ composition is comparable to that shown previously (83% TiOₓ) resulting in identical interface chemistry where the W 4f spectrum shows a composition of 90% WSe₂, 4% WSe₃, and 6% WOₓ. This suggests that repeatable interface composition is achievable under identical deposition conditions. The subsequent deposition of 2.4 nm of Ti metal, corresponding to the blue spectra, does not result in the formation of additional WSe₃ or WOₓ as the TiOₓ layer acts as a barrier preventing additional reactions with the top Ti layer.

3.2. Thermal boundary conductance
Thermal boundary conductance of the three different contact structures was measured with TDTR. The results are shown in figure 4. Deposition of Au/Ti contacts on the ~ 1 nm WSe₂/HOPG sample results in a value of hₓ of 22.2 ± 2.5 MW m⁻² K⁻¹. A second Ti-contacted sample, represented in the circle marker in figure 4, corresponds to ~2 nm WSe₂ which yields a much lower value of 6.77 ± 0.63 MW m⁻² K⁻¹. If we assume the resistances across the Ti/WSe₂ and WSe₂/HOPG to be the same in both samples, then the difference in hₓ is attributed to the difference in the thickness of the WSe₂ layer. Given the extremely low
Figure 2. (a) XPS spectra of the Se 3d and W 4f, and (b) Ti 2p core levels before and after the deposition of 2 nm TiO$_x$ on MBE WSe$_2$. A fit to the W 4f spectrum is shown in (c).

intrinsic cross-plane conductivity of WSe$_2$ [6, 7, 35] (up to two orders of magnitude lower than that of TiO$_x$), a film containing more WSe$_2$ layers is expected to cause the total interfacial conductance to decrease.

With the assumption that the Ti/WSe$_2$ and WSe$_2$/HOPG contributions to the total resistance are the same in the 1 nm and 2 nm WSe$_2$ samples, we calculate the difference in the resistance between the two samples to determine the effective difference in resistance between 2 nm and 1 nm of WSe$_2$. The result of the subtraction is 9.74 ± 0.15 MW m$^{-2}$ K$^{-1}$. With the assumption of a 1 nm WSe$_2$ layer, this equates to an effective thermal conductivity of ~0.01 W m$^{-1}$ K$^{-1}$. This value is close to the reported cross-plane thermal conductivity of 0.05 W m$^{-1}$ K$^{-1}$ for disordered WSe$_2$ [7]. For TMDCs grown by MBE it is well known that the layer adopt the rotational alignment of the substrate [35]. Since HOPG is highly polycrystalline azimuthally around the (0001) direction, the grown WSe$_2$ layers will be similarly polycrystalline. By analyzing the spacing between the nuclei observed by atomic force microscopy for MBE-WSe$_2$ studied in our recent work [36], we can infer that the grain size is likely on the order of 230 nm$^2$. Since our WSe$_2$ is polycrystalline, it is not surprising that this calculated effective thermal conductivity is on the same order of magnitude as the reported value. We note that the values are not directly comparable given that the reported value was directly measured by TDTR on a 62 nm thick WSe$_2$ film [7]. Nevertheless, our analysis highlights the dominating contribution of the intrinsic cross-plane resistance of WSe$_2$ to the measured value of $h_K$. Choi et al [37] have proposed that...
a high degree of bonding at the interface results in an increase in WSe$_2$/WSe$_2$ interlayer resistance due to a change in the phonon density of states (pDOS) of the top WSe$_2$ layer that is bonded to the metal. Bonding at the metal/WSe$_2$ interface is speculated to shift the pDOS toward that of the metal. This reduces the pDOS mismatch at the metal/WSe$_2$ interface, but increases the pDOS mismatch at the WSe$_2$/WSe$_2$ interface. This mechanism could also possibly explain the very low calculated effective thermal conductivity in our thicker Ti/WSe$_2$ sample. The effective thermal resistance in the work by Choi et al [37] is measured to be $4 \times 10^{-8}$ m$^2$ K W$^{-1}$ which equals 0.025 W m$^{-1}$ K$^{-1}$ at 1 nm thickness. This is very close to our calculated value.

The Au/TiO$_x$ contacts resulted in a lower $h_K$ value than the Au/Ti contact. This is likely due to the presence of WO$_x$ at the WSe$_2$/TiO$_x$ interface as well as the high measured thermal resistance at the Au/TiO$_x$ interface, a value of $9.91 \pm 1.07$ m$^2$ K GW$^{-1}$ [31]. The Au/Ti/TiO$_x$ contact to WSe$_2$ results in a slightly higher $h_K$ than the Au/TiO$_x$ contact. This is expected
Figure 5. The average resistance and the average Seebeck coefficient of the Au/Ti sample and the Au/TiO$_x$ sample versus measurement time. The solid symbols represent the resistance data and the empty symbols are for the Seebeck data.

given that the Au/TiO$_x$ interface is not present in this structure, and that the Ti/TiO$_x$ interface and Au/Ti interfaces exhibit a negligible contribution to the total resistance [31].

3.3. Seebeck coefficient and electrical conductance

The resistance and Seebeck coefficient data of the Au/Ti and Au/TiO$_x$ samples were averaged over measurements at four randomly selected locations across the sample surface so that the effects from non-uniformity of the HOPG substrate [38] and the film were minimized. The sample properties were monitored over a week to check for changes in behavior that occur as a result of the exposure to air and moisture in the measurements. In all cases the Seebeck coefficient is positive, indicating hole conduction.

As shown in figure 5, the Au/TiO$_x$ sample has a higher resistance compared to the Au/Ti sample. This is consistent with the thermal conductance measurements shown in figure 4 in which Au/TiO$_x$ interface has a smaller thermal conductance value and therefore larger thermal resistance value compared to Au/Ti interface. The larger resistance is due to the presence of TiO$_x$ layer which makes it more difficult for the electrons to tunnel from HOPG to Au. This is because the TiO$_x$ layer will likely provide a tunneling barrier between the Au and the WSe$_2$ valence band that is not present in the case of a Ti interlayer. We note that speculation of the exact barrier heights is avoided due to the large variability in the band gap [39] of TiO$_{2-x}$ species couple with the difficult in determining the exact stoichiometry of these ultra-thin layers. The resistance of the Au/TiO$_x$ sample remains relatively constant with time while that of the Au/Ti sample increases slightly, indicating that the Ti layer has gradually oxidized over time.

Since the WSe$_2$ films are less than three layers in thickness, tunneling is expected to be the dominant mechanism for electron transport. The tunneling Seebeck coefficient depends on the effective barrier height which in turn is a function of material work functions and layer thicknesses [40]. Specifically, the tunneling Seebeck coefficient depends on the logarithmic derivative of the WSe$_2$ density of states at the Fermi level which is pinned by the gold layer and hence it is independent of the intermediate (Ti or TiO$_x$) layers. In the current case, no significant difference between the two samples was observed. We conclude that there is negligible difference in terms of band alignment between the two interfaces and the two interfaces exhibit the same effective barrier height. This is consistent with the Au-WSe$_2$ band alignment being unaffected the presence of the Ti or TiO$_x$ interlayer. We note that the lack of peak shifts in the XPS core-levels after Ti or TiO$_x$ deposition suggested that no band bending was induced. In most samples, the Seebeck coefficient and the resistance have similar trends. In these samples, the resistance increases slightly over time, but the Seebeck coefficient decreases over time. However, we note that the changes in resistance and in Seebeck coefficient over time are minor.

We are unable to separate the resistance of the HOPG layer due to spatial fluctuations of the
resistance which results in large error-bars in resistance measurements. Compared to a metal, HOPG has a low electrical conductivity (2.0 $\times$ 10$^6$ S m$^{-1}$) along the graphene planes and 500 S m$^{-1}$ across the layers and therefore can affect the resistance measurements. If we use the current values, we obtain an equivalent interfacial figure of merit, $ZT = \frac{S^2 T}{\kappa}$, on the order of 10$^{-5}$ for the studied interfaces. Interfacial $ZT$ dominated by tunneling current is expected to be very small. While it is not the purpose of this work to make efficient thermionic devices, this result emphasizes that one needs to increase the number of 2D van der Waals layers to about 4–5 layers to suppress the tunneling effects and ensure thermionic transport [9].

4. Conclusions

We have characterized interface chemistry, interfactual electrical resistance, thermal conductance, and Seebeck coefficient of Au-Ti-WSe$_2$-HOPG interfaces. Ti metal exhibits strong reactivity with WSe$_2$ and results in a high thermal boundary conductance and low electrical resistance. TiO$_x$ exhibits some degree of reactivity and lower values of thermal boundary conductance and higher electrical resistance. Since the transport in this structure is dominated by tunneling, the equivalent thermoelectric figure of merit of the interface is small. The extremely small thermal conductance values along with the Ohmic nature of the contacts, make this interface an ideal interface for thermionic and thermoelectric applications. To make a practical thermionic device with reasonable efficiency, the active layer (WSe$_2$) needs to be thicker than those studied in this interface focused work. It is expected that the figure of merit significantly improves when 4–5 layers of WSe$_2$ are used.

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